

CHARACTERIZATION OF POLYMER DECOMPOSITION PRODUCTS BY LASER DESORPTION MASS SPECTROMETRY

Joan B. Pallix and Kenneth A. Lincoln
Eloret Institute
NASA Ames Research Center
Moffett Field, CA 94087
Phone: 415/604-0332, Fax: 415/604-0487

Charles J. Miglione, Robert E. Roybal and Charles Stein
Phillips Laboratory
Kirtland AFB, NM 87177-6008
Phone: 505/846-4798, Fax: 505/846-1926

Jon H. Shively
California State University
Northridge, CA 91330
Phone: 818/885-2166

SUMMARY

Laser desorption mass spectrometry has been used to characterize the ash-like substances formed on the surfaces of polymer matrix composites (PMC's) during exposure on LDEF. In an effort to minimize fragmentation, material was removed from the sample surfaces by laser desorption and desorbed neutrals were ionized by electron impact. Ions were detected in a time-of-flight mass analyzer which allows the entire mass spectrum to be collected for each laser shot. The method is ideal for these studies because only a small amount of ash is available for analysis. Three sets of samples were studied including C/polysulfone, C/polyimide and C/phenolic. Each set contains leading and trailing edge LDEF samples and their respective controls. In each case, the mass spectrum of the ash shows a number of high mass peaks which can be assigned to fragments of the associated polymer. These high mass peaks are not observed in the spectra of the control samples. In general, the results indicate that the ash is formed from decomposition of the polymer matrix.

INTRODUCTION

Materials retrieved from the long duration exposure facility (LDEF) have exhibited a wide variety of exposure induced chemical and physical surface modifications. Numerous investigations are underway to characterize the behavior of the various materials exposed from different locations on the satellite in order to identify the processes responsible for the observed effects. These processes may include complex interactions between the surface and atomic oxygen, UV or thermal radiation and/or chemical reactions with the products of outgassing. Surface properties were also affected by micrometeorite impacts and other contaminating particles.

The work presented here focuses on studies of several graphite/polymer matrix composites retrieved from leading edge and trailing edge positions on LDEF. A schematic diagram of the satellite is shown in Figure 1. The composite materials examined in this work were located in row 9, bay D (D09) on the leading edge and in row 3, bay D (D03) on the trailing edge of the satellite. While leading and trailing edge materials experienced similar exposure to solar radiation, there was a dramatic difference in exposure to atomic oxygen (AO) for panels in different locations on LDEF. The maximum total dose of AO received by the leading edge was on the order of 10^{22} atoms/cm² while the minimum on the trailing edge was only about 10^4 atoms/cm².

The long term goal of this particular study is to determine the origin of the ash-like substance found on the surfaces of polymer matrix composites (PMC's) exposed on the leading edge of LDEF. The preliminary work presented here involves the initial characterization of the surfaces of several leading and trailing edge PMC's by laser desorption mass spectrometry and by electron microscopy (SEM and TEM). The three composite materials of interest C/polysulfone, C/polyimide and C/phenolic, are considered dark body composites because of their black carbon fiber matrices. Initial inspection of PMC's indicated that the dark body composites placed on the leading edge of LDEF experienced erosion as well as an "ashing" effect of the excess resin layer on the sample surfaces. Samples placed on the trailing edge of LDEF did not experience the ashing effect but did show slight surface blistering. Light body composites, such as 3D-quartz phenolic placed on the leading edge displayed no ashing behavior but did experience erosion of the surface resin. The silica reinforcement fibers underwent no noticeable erosion. Trailing edge 3D-quartz phenolic produced no observable erosion or blisters.

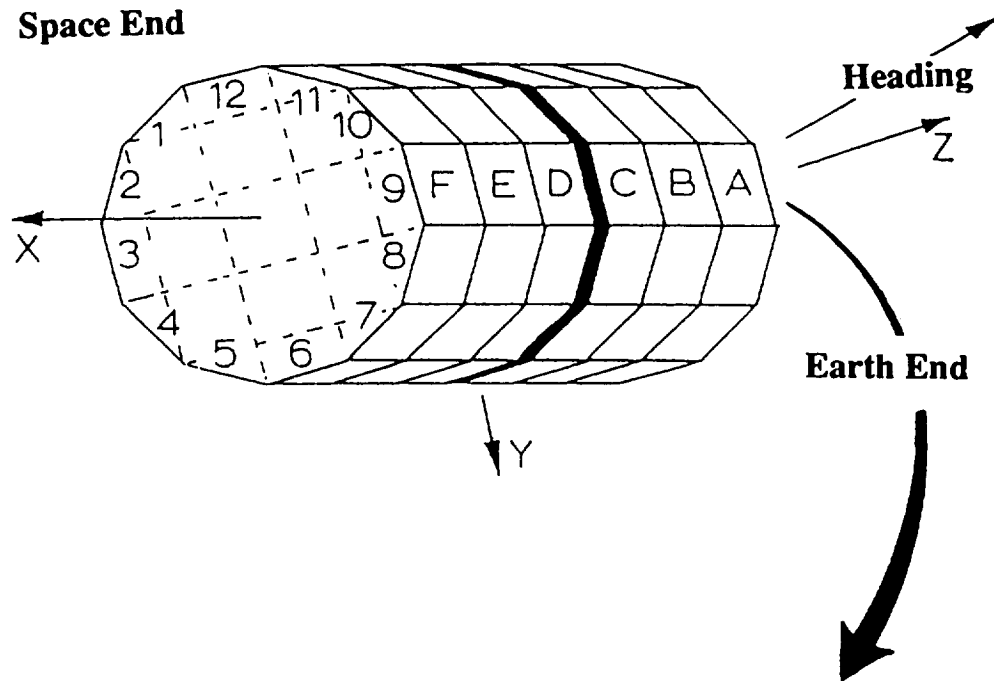


Figure 1. Schematic view of LDEF showing orientation and tray notations.

SEM images of the carbon reinforced composites were typical of those reported previously by other research groups (refs.1-4). The erosion process has caused cone type formation on the surfaces of leading edge samples and the ash appears in clumps that have a "cobweb"-like appearance. The level of ash on the C/polyimide was much higher than on the C/polysulfone. As reported in other work, there is erosion of both resin and top ply fibers in many areas of the C/polysulfone composite and in a few isolated areas of the C/polyimide. The observed differences in fiber damage may be due to differences in thickness of the surface resin layer on the two composites and/or the differences in polymer erosion rates. The SEM cross-sections show that the erosion does not extend deeper than ~80 microns into the carbon fabric of the C/polysulfone and ~35 microns into the top ply of the C/polyimide.

It is not clear why the delicate ash-like material remains on the surfaces of leading edge composites rather than being removed by AO erosion. It is also unclear why the silica reinforced materials with the same matrix polymers experience erosion but no ash is found on the surfaces. Possibly, the extreme differences in emissivity (and resulting temperature differences) of the different reinforcement materials plays a role in formation and/or removal of the ash. Surface impurities may also play a role.

Preliminary studies of three graphite reinforced PMC's have been made using time-of-flight mass spectrometry to help determine the composition of the surface ash. The many advantages of time-of-flight (TOF) mass spectrometry for surface analysis are well known. For this work, the technique is particularly useful due to the small amount of material available for analysis and the fact that no sample preparation (or modification) is required. In our instrument, surface material is removed directly by laser desorption. With laser desorption, electrically insulating materials are much less susceptible to surface charging which can cause detection problems when using ion beam or electron stimulated desorption. Desorbed neutral species are subsequently ionized by electron impact and accelerated into the TOF analyzer. The entire mass spectrum is collected for each laser pulse which minimizes sample volume requirements. Another advantage of this method is that electron impact is a nonresonant ionization process which means that no one species will be selectively ionized leading to ambiguous data interpretation.

Energy dispersive x-ray (EDX) and electron diffraction techniques have been used in conjunction with the mass spectra to identify inorganic contaminants. Because of the relatively large number of peaks observed mass spectra of organic materials, it is often difficult to identify inorganic contamination due to mass interferences (i.e., Si and CO at mass 28 or S and O₂ at mass 32). In addition, using laser desorption, some inorganic species may not be removed from the surface as efficiently as the organic material. As will be discussed later, EDX results have revealed a number of surface contaminants that were not apparent in the mass spectra. Macroscopic and scanning microscopy results have been presented elsewhere and will be published in the Journal of the International Metallographic Society in January 1993.

EXPERIMENTAL

The laser desorption mass spectrometer used for this work is shown in Figure 2 (ref. 5). The instrument was developed around a Bendix TOF analyzer at NASA Ames Research Center (Thermal Protection Materials Branch). The desorption laser is a non-Q-switched Nd:YAG with a pulse width of ~300 microseconds (μ s). The neutral portion of the vapor cloud produced by the laser travels in a line-of-sight path directly into the region of 70 eV electron impact where ions are formed.

Any ions emitted directly from the surface are deflected in a 1000 V field before they are able to reach the electron interaction region. The extractor of the TOF spectrometer can be pulsed at a repetition rate of up to 50 kHz so that a complete spectrum of the transient vapor cloud is collected every 25 to 100 μ s resulting in a mass spectral array. In this work, 15 mass spectra are obtained for each laser pulse and these are averaged for the final plots. The data collection system consists of an 8 bit, 100 MHz Transiac transient digitizer with averaging memory (CAMAC system).

The laser beam is focused to a spot size of \sim 4-mm diameter in order to keep the photon flux relatively low to minimize production of small organic fragments during desorption. Spectra containing only low mass generic fragment peaks are not very useful when trying to characterize organic materials. SEM images were obtained before and after desorption to ensure that the ash was being removed. Desorption of ash is observed using pulse energies as low as 100 mJ/pulse (<1.3 kW/cm²) but no signal was observed from the bulk C/polymers at energies below \sim 250 mJ/pulse. In order to carry out all experiments under the same conditions it was necessary to use the higher laser power. Note that due to cross linking and/or intertwining of high molecular weight polymer chains, it is difficult to remove material from the surfaces of bulk polymers without also causing significant fragmentation. This is a general problem for any surface sensitive technique used to generate characteristic mass spectra of bulk polymers. While characteristic spectra can be obtained, they typically contain peaks at masses below 500 amu. Also note that the ionization process itself can cause additional fragmentation of the desorbed species. In future work we will use a CO₂ laser for desorption and the postionization will be accomplished using vacuum ultraviolet laser radiation at 118 nm. Ionization with VUV has proven to be an effective method for providing efficient ionization while avoiding further fragmentation of desorbed organic polymer species (ref. 6).

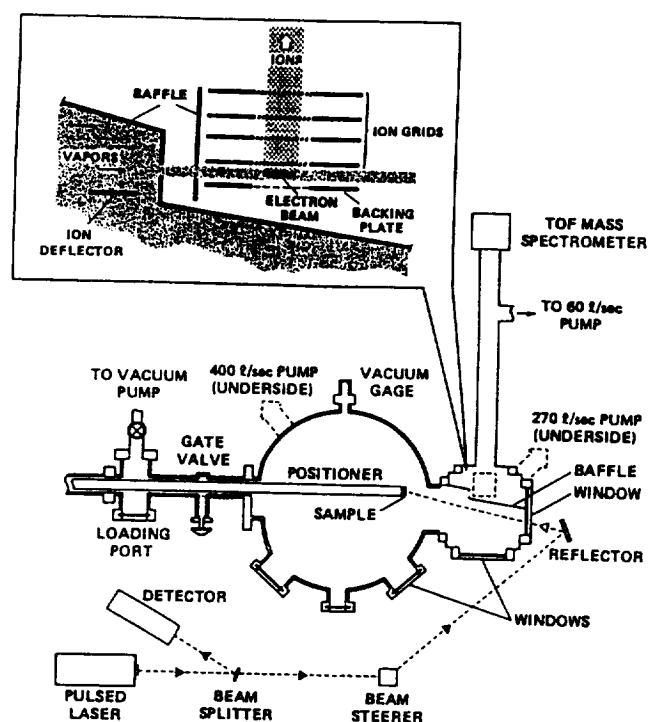


Figure 2. Schematic representation of the laser desorption time-of-flight mass spectrometer.

RESULTS AND DISCUSSION

The first step in understanding the origin of the surface ash observed on the three leading edge PMC's was to determine if the ash was different for each sample. If it had the same composition on all three samples it would clearly have resulted from the deposition and/or reaction with some general contaminant (i.e., species outgassing from the satellite). Mass spectra of the surface ash observed on the C/polysulfone, C/polyimide and C/phenolic are shown in Figure 3. The mass peaks above ~ 100 m/z units are the most useful for making a comparison. A cursory comparison of the three spectra indicates that all of the surfaces have different compositions and this could not result from the same source of contamination.

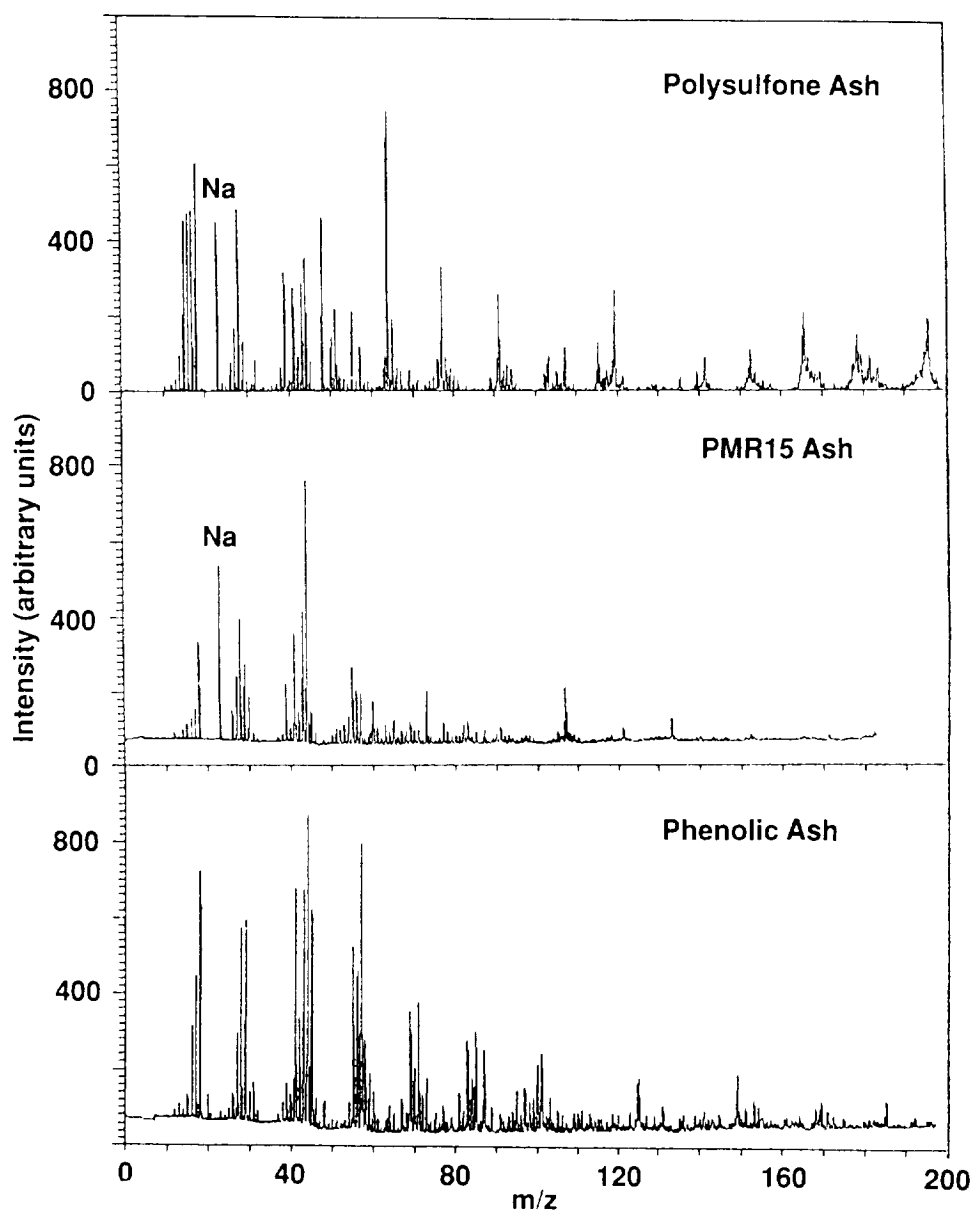


Figure 3. Comparison of mass spectra obtained from three leading edge polymer matrix composites.

Note that no significant peaks are present in the ash spectrum that are characteristic of graphitic carbon (i.e., C_2 or C_3). Electron diffraction studies also show that the ash consists only of amorphous C. No crystalline forms of carbon are found in the surface ash. There is a large Na peak in the surface ash spectrum of both C/polysulfone and C/polyimide which was not observed on the C/phenolic. EDX analysis of all the control samples show a very low level of Na and Si. However, these contaminants observed on exposed samples appear to have come from some source external to the sample because they are observed at much higher average surface concentrations than on the controls. Other inorganic contaminants were detected in the EDX spectra of both leading and trailing edge samples. These include F, Mg, Al, Si, S, Cl, Ca, K, Ti, Cr, Fe and Ni which were not necessarily distributed uniformly over the surfaces. In addition to these contaminants, the leading edge samples were also contaminated with P, Zn, Ga, As, Mo, Ag, Au, and Pb. The sources of most of the contamination particles can be attributed to scattered debris from nearby materials on the tray (i.e. Ga-As, Ag coated Teflon) and outgassing of lubricants and adhesives on the satellite. General discussions of contamination (organic and inorganic) on LDEF and other spacecraft have been presented elsewhere (refs. 7-9).

Figures 4 and 5 give structures for the components of the polysulfone and the PMR15 (polyimide) respectively. The Figures also compare the mass spectra of the bulk control samples with those of the leading edge LDEF samples in the surface ash and the bulk. The top frame shows the mass spectrum of the ash which, in both cases, contains high mass peaks that can be assigned to fragments of the respective matrix polymers. Although all of the high mass peaks have been assigned, only some of them are shown in the polysulfone spectra. The other tentative peak assignments are given in Table 1 for the polysulfone ash. Note that for both samples, the total intensity of the ash spectrum is at least 5 times higher than in the layer beneath the ash or in the control. A high desorption yield is typical for species that are not strongly bound to the surface. Although the surface coverage of the ash is not uniform and some of the pure polymer may be exposed on the surface, the majority of the signal observed in the "ash" spectrum is due to the ash and not the pure polymer. As mentioned previously, it is difficult to remove intact high molecular weight polymer chains from a bulk sample by any means (laser desorption, ion or electron stimulated desorption). The fragmentation resulting from desorption and ionization processes are responsible for most of the peak intensity being observed at masses below 100 m/z units.

SEM images show that the "ash-like" material has been removed from the surface after one or two laser shots. On the polyimide composite, 15 to 20 additional laser shots were required to remove the remaining surface resin and fully expose the bulk material. The mass spectra shown in the center frames of Figures 4 and 5 are obtained in the bulk of the PMC's. These spectra show characteristic carbon fiber peaks at $m/z = 12, 24$ and 36 as well as peaks characteristic of the polymers. This is clearly obtained from the bulk C/polymer and compares well with the bulk of the control sample. For these experiments, the surfaces of the control samples were scraped with a clean razor blade to be sure that a spectrum of the bulk material was obtained. This is common practice for studies of bulk polymers and is important in order to avoid collecting spectra of surface reaction products which will not be characteristic of the bulk polymer itself. In general, the peak assignments for C/polysulfone and C/polyimide suggest that the ash formation results from exposure induced decomposition of the matrix polymer.

Table 1. Tentative assignments of notable mass peaks in the polysulfone ash spectrum.

15	CH ₃	77	C ₆ H ₅
18	H ₂ O	91	C ₆ H ₅ -CH ₂
23	Na	107	O-C ₆ H ₄ -CH ₃
28	CO	119	C ₆ H ₅ -C(CH ₃) ₂
32	S	141	C ₆ H ₅ -SO ₂
44	CO ₂	166	C ₆ H ₅ -C-C ₆ H ₅
48	SO	170	C ₆ H ₅ -O-C ₆ H ₅
64	SO ₂	181	C ₆ H ₅ -C(CH ₃)-C ₆ H ₅
		196	C ₆ H ₅ -C(CH ₃) ₂ -C ₆ H ₅

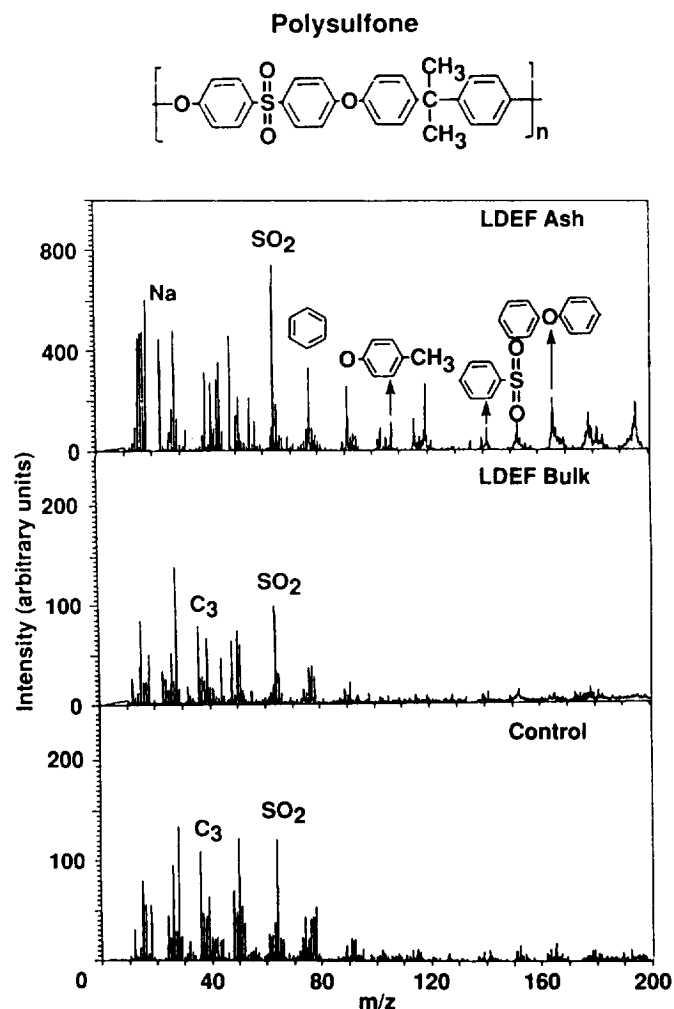


Figure 4. Comparison of mass spectra of polysulfone control sample (bottom) to the leading edge LDEF sample in the ash (top) and in the bulk (center).

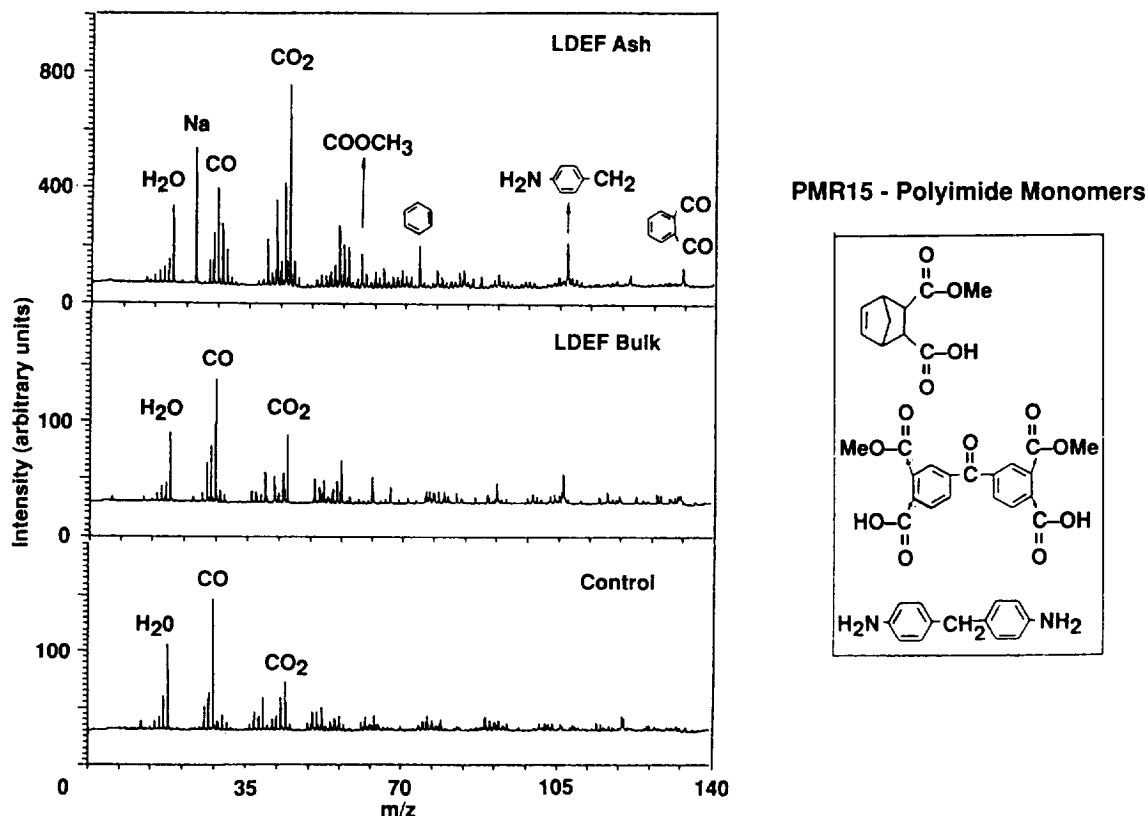


Figure 5. Comparison of mass spectra of polyimide (PMR15) control sample (bottom) to the leading edge LDEF sample in the ash (top) and in the bulk (center).

One important experimental question to answer is : How do we know that the optical properties of the ash (which is dull black) are not different than the control sample (which is shiny black) at 1.06 microns? If the leading edge samples absorb significantly more photons than the control samples then surface heating or energy redistribution effects might cause decomposition of the polymer under the ash giving rise to some of the observed mass peaks. To confirm that this is not occurring, two experiments were done. First, the infrared reflectance spectra were obtained for the C/polysulfone leading edge and the control sample. The samples showed similar reflectance (within 1 percent) at 1.06 microns. In the second experiment, mass spectra were obtained from the control samples at a higher laser power (factor of 3) than that used for the previous measurements. This was done to see if the resulting spectrum was similar to the spectrum of the ash. This was not the case as shown in Figure 6. As expected, the high laser power caused extensive fragmentation for polysulfone and phenolic and the strongest signals were produced from species below $m/z = 100$. Surprisingly, the PMR15 spectrum obtained at high power shows four very intense high mass peaks. Three of these peaks are also observed in the ash spectrum but at very different relative intensities. It is interesting to note the different fragmentation patterns resulting from the two different methods of fragmentation (i.e., exposure on LDEF vs. laser ablation at 1.06 microns). The results of the IR analysis and the high power study indicate that peaks observed in the ash spectra (above ~ 100 m/z) are not due to desorption of the intact bulk polymers.

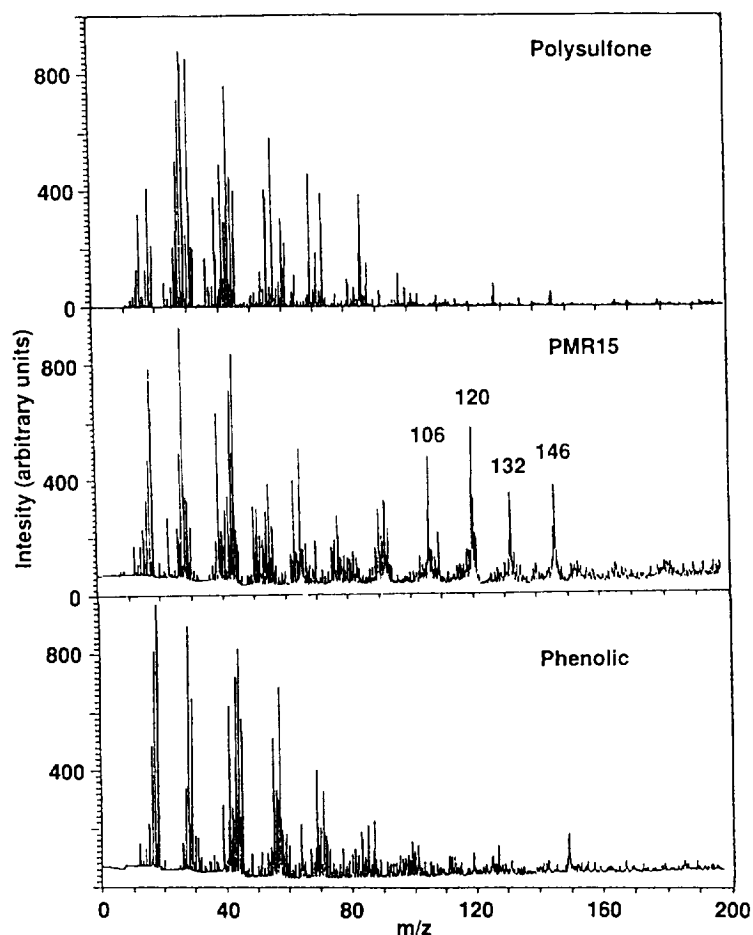


Figure 6. Mass spectra of control samples obtained at high laser power (800 mJ/pulse).

In the final study, a comparison was made of the mass spectra obtained from the surfaces of the control samples and the LDEF trailing edge composites. Although the control samples were essentially "unexposed," surface reactions can occur in any environment and even the control resins may have a different composition at the surface than in the bulk. The trailing edge mass spectra appear very similar to the control samples indicating that no extensive polymer degradation other than blistering occurred on the trailing edge as a result of exposure on LDEF. This indicates that the ash formation depends on the dose of AO (and/or other particle bombardment) and possibly on synergistic effects.

CONCLUSION

This preliminary study has shown that the ash observed on leading edge graphite reinforced PMC's contains both organic and inorganic contaminants. For the PMC's studied, a significant effect of exposure on LDEF was the erosion and decomposition of the surface resin. Erosion of both the resin and the reinforcement fiber was observed in the C/polysulfone, but for the C/polyimide it was primarily the surface resin that was affected and not the bulk material underneath. The ashing effect occurred only on leading edge samples while trailing edge samples underwent no observable

changes in surface composition relative to the control samples (although there was evidence of surface blistering on graphite reinforced composites).

It has not been the goal of this preliminary work to identify the causes of the observed material behavior but to simply make a preliminary characterization of the effects of prolonged exposure in low Earth orbit. This initial empirical evaluation is essential for determination of long-term material performance. A complete surface characterization would include studies of optical, compositional, crystallographic, morphological, and mechanical properties. This information alone cannot lead to definitive mechanistic conclusions but could aid in the development of laboratory experiments designed to reproduce the observed material dependent effects. Determination of the synergistic mechanisms responsible for material modifications will require a much more extensive future effort. In future work, experimental attempts to reproduce the erosion and ashing effects on these PMC's will include sample exposure to a source of low energy AO and other particles in conjunction with UV, VUV and/or IR radiation. The general need for these studies has long been recognized and this type of work is currently underway in other laboratories (ref. 10). Subsequent to ground-based exposure, mass analysis of polymer decomposition products may be helpful in the elucidation of erosion and depolymerization mechanisms. If mechanistic information is to be extracted from the mass spectra, the peaks of parent fragments existing on the composite surface must be observable. To achieve this goal, a CO₂ laser will be used for desorption and VUV laser radiation for "soft" ionization. In addition, efforts will be made to understand why the ash is not eroded from the surface by AO and why no ash is observed on silica reinforced composites.

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